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PAPER 5

IT'S HOW YOU PLAY THE GAME: Design of an Electronic Assistant for Organic Qualitative Analysis.

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ABSTRACT: Organic qualitative analysis is an invaluable segment of our laboratory curriculum, providing an intensive review of techniques and exercising the students' powers of observation and deduction. However, grading the work of 275 students each having up to six unknowns is a time-consuming process for the instructor. In response to this problem, a computer program design is proposed which will provide the rapid, high-level feedback on empirical findings required for the students' success in these experiments. While the program is designed to assist by giving the students a critique of their technique and a confirmation of their findings, it must necessarily be designed carefully to require the the laboratory work actually be carried out by prohibiting blind guessing ("dry labbing"). All aspects of such a program's design and its implications will be discussed.

I. INTRODUCTION: Qualitative analysis remains in the sophomore organic chemistry laboratory curriculum for its emphasis on observation and deduction. For the greater than 75% of Northwestern University students taking the course in preparation for medical school, the analogy is made between making observations on an unknown compound and deducing its identity and making observations on a patient and deducing a diagnosis for treatment. The laboratory practice and thinking skills are a useful review of the whole laboratory course.

II.A. QUAL AT NU: The students are set a series of unknowns in three categories: (I) oxygen functional groups in oxidation states I and II (alcohols, aldehydes, ketones, enols and phenols); (II) carboxylic acid derivatives (acid chlorides, anhydrides, esters, amides and nitriles); and (III) a list of 24 to 32 compounds all of which are liquids boiling within a 10-degree range, i.e. not readily distinguishable by boiling point determination. These last include all of the prior groups, as well as amines, hydrocarbons, ethers, alkyl and aryl halides, nitro compounds and free carboxylic acids. By dividing the unknowns in this manner, the set of tests which must be prepared for each lab is limited to a reasonable size.

B. Inherent in the design of the experiments is the expectation that the students will succeed quickly if they have mastered the process of careful experimental technique and good observations. At the same time, qual will present a challenge to even the best of the students,

obviating the operation of "luck" in the identification process.

C. In the first set of unknowns, the students are introduced to the importance of accurate boiling point, melting point, and solubility data, and the operations of functional group tests and derivative formation. This set of compounds yields the fastest, most definitive tests of the group and serves to practice the skills needed to go on in qual. The second group of unknowns are keyed to their parent carboxylic acids, all of which are stable, solid acids and may be obtained by hydrolysis of the unknowns. In this set, good pH change observations are crucial.

D. The last set of unknowns, called "strategy", is designed as identification from a limited list of options, i.e. five or six (binary) decisions to uniquely identify one of thirty-two compounds. The potential to explore some of the more ambiguous tests is present in strategy, but a well-developed strategy based on solubility, pH change and simple tests will identify most of the candidates. Needless to state, strategy separates the quick from the dead after two quarters of organic laboratory.

III. A. GRADING QUAL: Standard compounds are provided and the students are actively encouraged to run blanks for benchmark observations of the tests. The teaching assistants are grading the students on basic technique, record keeping, willingness to work through problems, and application of what they have learned in their previous labs. The accuracy of their identifications of the unknowns is graded separately, and the TA's do not know the specific identities of the students' unknowns.

B. The outcome of their qualitative analysis is graded via "guess sheets" wherein the students list the physical properties they have found, note critical observations and then "guess", in an educated mode, the identity of their unknowns. These guess sheets are graded by the instructor, the only person knowing the identities of the compounds. Grading includes giving hints where the empirical data is outside the range expected for the particular compound. Each of the unknowns may be "guessed" two or three times before the student is told to stop work on the problem.

IV. THE PROBLEM AND A SOLUTION: Problems arise from the intensive handling of the qual guesses. In a large lab, there may be up to 275 students, each submitting one to three guesses on each of four to six unknown compounds. The delay between submittal and return of graded guesses is kept under 24 hours, but restricts the flexibility the student can use from rapid feedback in the guessing process. In response to this need, a computer program could be constructed would (1) track each of the students working on the qualitative analysis scheme; (2) provide a rapid feedback cycle on the goodness of data obtained for the various tests and (3) critique the students' approach to each unknown.

V. A. THE PROGRAM DESIGN: The qual assistant program will have three functions - searching a reference database, responding to the students guesses and grading with maintenance of "security". The reference database (RDB) will be a list of organic chemicals and accompanying lists of properties, including alternate names, molecular formulas,

boiling or melting points, colors, odors, solubility and pH effects in water, functional groups present, reactivity with various test reagents, possible decomposition or problematic reaction products and physical properties of useful derivatives.

B. The data base would include structures of the compounds--atom and bond tables such as are used in Beaker. These may be interpreted and drawn by a program routine, allowing the students to search the database by structures and infer reactivity from structures. Spectroscopic data including ir and ¹Hnmr absorptions, possibly uv and ¹³Cnmr will be included as well. The spectra would likely be presented as simple lists and not as their images, but could be easily cross-referenced to a CD-ROM collection of images where the hardware resources are available.

VI. A. DESCRIPTION OF PROGRAM OPERATION: Communication with the student-user would be handled by two parts of the program. First would be a "query engine" which would present a series of questions to the user, as well as lists of options from which to choose some of the answers. Specific data, such as identification numbers and boiling or melting points, would be typed in. The query engine would follow a fixed routine, presenting questions, reading the answers and writing a list of the student's empirical data parallel to the values in the RFD. This list would be the input for the second, more active, part of the assistant.

B. The second part--the core processor--would read the list of student values and RFD values and make qualitative comparisons of the information. "Judgment calls" on the usefulness of the various data presented by the student would be made with considerations of qualitative usefulness being indicated by fuzzy response value terms. The responses would be coupled to ranges calculated around the listed values, i.e. a value 5% low would be "somewhat low" where a value 25% low would be "extremely low". These responses would be presented to the student through the query engine.

C. The goodness of the student's data would be used to generate a score for the student's work on the unknown. The data which the student has put into the program could be altered up to the point where the student actually makes a "guess", at which point a preliminary score is written on the user's record. In a second or third guess on a single unknown, the core processor may change the user's score by noting improved the data and a refined the guess. The score will be "fixed" when the guess is correct or the user has run out of guesses.

D. As part of the feedback process, the particular list of data presented by the student may be critiqued by the program using the scoring logic. The program may ask for important pieces of information which are missing during a student's inquiry, and it will indicate, within reason, when a student's data are not accurate enough to be usable.

E. To prevent a student from fabricating data and carrying out a blind guessing process, the feedback messages will be reserved until a larger collection of information is available indicating that the data are consistent with a single compound. The feedback messages will be

varied so that their intent is clear, but their "switching" levels are not apparent, i.e. an erroneously low boiling point reading may be "extremely low" or "exceedingly low", or "very, very low", to keep the students from correlating "very" with 10% low and "extremely" with 25%, etc. Correction of previously entered erroneous data will be allowed, but writing and rewriting data using the feedback cycles to "cook" responses will be intercepted by an examination of the pattern of the students' responses.

VII. A. CONFIDENTIALITY OF INFORMATION: The controller program would control access to and record transactions in the other program workspaces. This would consist of three smaller databases: the first being a class list of students' names and some identifying numbers. A password or alias may be chosen by the student while using the program and appended to this list, but the list itself would be unavailable to the student users. A second list would be invisible to the user--the "key" list of the identifying numbers of the unknown samples and their identities which would be read only by the program. A third list would be written by the program, and consist of the student's identity, the unknown compound's number and actual identity, the listed values for the compound, and the student's responses to questions which should correspond to those values, the number of inquiries which have been made on this sample, and a score. Some of this information would be presented to the student on request, some would again be invisible.

B. The class roster and the list identifying the unknowns would be entered by the course instructor using access routines in an instructor's area of the program. The reference data base--the main body of information about organic compounds--could also be expanded or modified by the instructor. The particular set of questions asked and the basis for scoring could also be altered, but with greater effort. However, frequently used alternatives, such as inclusion or omission of spectroscopy data, could be "toggled" in and out of the set.

VIII. FIGURE: Figure 1. is a diagrammatic depiction of the various areas of the program and their relationships to each other. Arrows indicate a direction for one area writing in another. Read-only is possible in the direction opposite the arrow. (The diagram is a PICT file created in DeskDraw and is a simple monochrome outline diagram.)

IX. A. USING A COMPUTER PROGRAM AS A GRADER: The Qual assistant is designed to lift the burden of grading qualitative analysis for larger classes, and allow the instructor to have more time with the students themselves rather than their written work. At the same time, having a machine capable of grading focusses the students' attention on the machine. It is imperative that the process of analyzing the unknowns and carrying out the test be made as lively as possible so that the opportunities to learn from empirical data and become skillful with "hands-on" work be made the most of.

B. The program and its machine container will be subject to "hacking" by the technically more enterprising students. Control of the flow of information (reading and writing processes) is part of the design of the program. At the same time, it may be necessary to have encryption routines built into these same routines so that the contents may not be altered without detection. The program will not be written in a

high level, so that ready access to even the reference data base will be made difficult thus directing the students to the laboratory and the instructors for more contemplative and interactive work.

C. The highly structured nature of the program may be a weakness as well as a strength. The set of questions presented by the program rigidly directs the students' activities in the laboratory, and rivets their attention when using the machine. This same effect is seen at any point where a "worksheet" must be filled out. Scoring of laboratory work will be focussed on key tests for qual: solubility, pH effects, boiling and melting points and, alternately, spectroscopic data.

XI. IMPLEMENTATION: The Qual Assistant design is beyond the capacity of programmable databases in design. Consequently, the program will be written in a high-level language (C/C++) using only those data base functions which it requires and bypassing the fancier built-in functions in commercial programs such as Double Helix. Using the high-level language has the added advantage of making the program small and fast in comparison to a similar programmed database, allowing it to run on a small machine with a minimum capacity in memory.

B. The Query Engine and the Core Processor would take two programmers six months to a year to construct, and the Reference Data Base the same time with several people working to collate the information from various reference, catalog and textbook sources. Inclusion of safety, hazard and storage data will make the data base useful beyond the Qual Assistant program. Testing and refinement of such a program would require several cycles through classes requiring a year or more. The design of the program does not parallel the design of the NU laboratory curriculum so closely that it may not be used at other schools. Consequently, wider dissemination of the program would be expected in due course.

XI. APPENDICES: Three Appendices are included with the text of this paper. The first two are scenarios of students interacting with the Qual Assistant to determine the identity of two different compounds. The scenarios do not include either spectroscopic information or structural formulas. The third appendix is a "paper" version of the questions used for the lab preparation.

XII. QUESTIONS FOR DISCUSSION: In paragraph IX C, I describe a "worksheet effect" where a set list of questions channels the students thinking and activities in lab. What alternative would require the students greater participation in framing the questions to be asked and finding the answers to their own questions?

B. Black boxes: I think that students view that running instruments makes them feel more sophisticated, more "scientific", more attuned to an undesirable mystique. I want them to learn that "doing chemistry" does not require the black boxes. I design the curriculum in the service laboratories to focus the students work on observations and records knowing that professional schools for most of my students and advanced chemistry courses for others will, in time, have them running many instruments. I feel strongly that the students must learn to think about what they have themselves seen before they can interpret

what some instrument has "seen" for them. The qual scheme is "wet lab" only for this reason, excluding use of ir and nmr for most students. I invite comments on the role of qualitative analysis and use of instruments as part of this discussion.

Appendix A: an example of scenario of proper use.

Student A: unknown 111 on a first guess. This example is of an "easy" unknown with good data input.

The program would identify the student, then identify the unknown; it would then check to see whether this is a first or second unknown in this category, and whether it is a first or second guess on this particular compound.

*is the sample solid (s), or liquid (l) at room temperature?

>l

*What boiling point have you determined for this compound? (Write a number or x if undetermined)

>183

*Is the sample colored as a pure compound? (n/y)

>clear

*Is that yes (y) it is colored or no (n)?

>n

*Do you have an observation on the odor of the compound (y/n)?

>n

*What is the approximate solubility of this compound in room-temperature water: miscible (m)/ soluble (s)/ slightly soluble (d)/ insoluble (i)?

>i

*What is the pH of the water which was exposed to the compound in the solubility test: basic (b) if >10/ slightly basic (s) if >7 but <10/ neutral (n) if pH is unchanged/ slightly acidic (v) if pH >4 but <7/ acidic (a) if pH <4/ not determined (x) ?

>x

*Is the compound more soluble in sodium bicarbonate solution (y/n/x)?

>x

*Is the compound more soluble in sodium hydroxide solution (y/n/x)?

>y

*Was the solubility reduced by readjusting the pH back to 7 after adding hydroxide (y/n/x)?

>x

*Type in the numbers (separated by commas) of all the tests which you tried on this compound for which you have observations:

- | | |
|----------------------------|---------------------------|
| (1) hydrolysis in water | (2) rxn w/ acidic Cr(VI) |
| (3) hydrolysis in base | (4) rxn w/ Ce(IV) |
| (5) hydrolysis in acid | (6) rxn w/ Fe(III) |
| (7) rxn w/ Ag+ | (8) rxn w/ HCl/ZnCl2 |
| (9) rxn w/ Br2 in water | (10) rxn w/ 2,4-DNP |
| (11) rxn w/ iodine in HO- | (12) rxn w/ hydroxylamine |
| (13) rxn w/ NaI in acetone | (14) rxn w/ semicarbazide |
| (15) rxn w/ Fe(Fe(SCN)6) | (16) rxn w/ AlCl3/CHCl3 |
| (17) Rxn w/ PhSO2Cl | (18) rxn w/ Mg/ether |
| (19) rxn w/ Cu/flame | (20) rxn w/ Br2/CCl4 |
| (21) rxn w/ MnO4- | (22) rxn w/ Fe(OH)2 |
| (23) ignition | (24) rxn w/ HNO3/H2SO4 |

(25) rxn w/ 3,5-dinitrobenzoyl chloride

(26) rxn w/ benzoyl chloride

>9, 2, 4, 10

*On reaction with bromine in water, did you observe any of the following: precipitate (p)/ decolorization (d)/ formation of oily layer (o)/ heat evolved (h)/ nothing (n)?

>d, p, h

*On reaction with chromic acid, did you observe any of the following: solution turned dark (d)/ solution turned clear (c)/ green precipitate (g)/ brown precipitate (r)/ black material present (l)/ no change (n)?

>d, l

*On reaction with ammonium cerium(IV) nitrate were any of the following observed: solution decolorized (d)/ solution turned red (r)/ white solid precipitated (w)/ colored solid precipitated (c)/ solution heated up (h)/ no reaction (n)

>r

*On reaction with 2,4-dinitrophenylhydrazine, was a precipitate formed (y/n)?

>y

*Was the precipitate red (r)/ orange (o)/ yellow(y)?

>r

*Was the precipitate filtered out of the solution? (y/n)

>y

*Was the precipitate recrystallized (y/n)?

>n

*Was a melting point obtained for the precipitate (y/n)?

>y

*At what temperature did the compound finish melting (all liquid)?

>218

*Do you wish to run through the list of questions to correct your responses (y/n)?

>n

*Type all the numbers which correspond to the functional groups you believe may be present:

- | | |
|---------------------|---------------------------|
| (1) alcohol | (2) aldehyde |
| (3) enol | (4) ketone |
| (5) phenol | |
| (6) carboxylic acid | (7) acid chloride |
| (8) acid anhydride | (9) ester |
| (10) amide | (11) nitrile |
| (12) amine | (13) nitroalkane |
| (14) ether | (15) alkane |
| (16) alkyl halide | (17) alkene/alkyne |
| (18) aryl halide | (19) aromatic hydrocarbon |

>5, 4, 2

*Which table would you like to examine first: phenols (4), ketones (3), aldehydes (2), none (n) ?

>3

*You observed a boiling point of 183 for this compound: what range of boiling points do you want to see?

>183-200

-->this would be a display from the database<--

ketone	bp	dnp mp	oxime mp	semi-C mp
ethyl acetoacetate	181	93		133
5-nonanone	186			90
3-nonanone	187			112

2,5-hexanedione	194	257	137	224
2-nonanone	195	56		119
acetophenone	202	240		199

*Do you wish to choose one or look again (c/a) ?

>a

*Do you wish to look at the same table again or go to a different table (s/d) ?

>d

*Which table: phenols (4), aldehydes (2), none (n) ?

>2

*You observed a boiling point of 183 for this compound: what range of boiling points do you want to see?

>183-210

-->this would be a display from the database<--

aldehyde	bp	dnp mp	oxime mp	semi-C mp
benzaldehyde	179	237	35	222
nonanal	185	100	64	100
glutaraldehyde	189		178	
phenylacetaldehyde	194	121	100	153
salicylaldehyde	197	252	63	231
m-tolualdehyde	199	195	60	204
o-tolualdehyde	200	194	49	209
p-tolualdehyde	205	234	80	234
decanal	207	104	69	102

*Do you wish to choose one or look again (c/a) ?

>c

*You may choose two: type in the names carefully below:

>salicylaldehyde, p-tolualdehyde

*You have correctly guessed the identity of compound 111!

*Do you wish to work on another compound (y/n) ?

>n

Appendix B: a scenario of the program in use.

Student B: unknown 201 on a first guess. This is a difficult unknown with data which is not entirely good.

The program would identify the student, then identify the unknown; it would then check to see whether this is a first or second unknown in this category, and whether it is a first or second guess on this particular compound.

*is the sample solid (s), or liquid (l) at room temperature?

>l

*What boiling point have you determined for this compound? (Write a number or x if undetermined)

>155

*Is the sample colored as a pure compound? (n/y)

>y

*What color is the compound: yellow (y)/ beige (b)/ brown (r)/ black (l)/ red or reddish (r)/ orange (o)/ other (x)?

>y

*Is the color pale(p) or intense(i)?

>p

*Do you have an observation on the odor of the compound (y/n)?

>y

*Can the odor of the compound be described any of the following (list the numbers of all you want, separated by commas):

(1) sweet (2) fruity (3) turpentine (4) gasoline (5) pungent (stinging) (6) vinegary (7) meaty (8) spicy (9) stench (gas) (10) rotten (dead fish) (11) fatty, waxy (12) floral (13) nutty (14) hot plastic upholstery (15) no discernible smell (16) indeterminate smell

>14, 4, 11

*What is the approximate solubility of this compound in room-temperature water: miscible (m)/ soluble (s)/ slightly soluble (d)/ insoluble (i)/not determined (x)?

>d

*What is the pH of the water which was exposed to the compound in the solubility test: basic (b) if >10/ slightly basic (s) if >7 but <10/ neutral (n) if pH is unchanged/ slightly acidic (v) if pH >4 but <7/ acidic (a) if pH <4/ not determined (x) ?

>x

*Is the compound more soluble in sodium bicarbonate solution (y/n/x)?

>x

*Is the compound more soluble in sodium hydroxide solution (y/n/x)?

>y

*Was the solubility reduced by readjusting the pH back to 7 after adding hydroxide (y/n/x)?

>x

*Type in the numbers (separated by commas) of all the tests which you tried on this compound for which you have observations:

(1) hydrolysis in water (2) rxn w/ acidic Cr(VI)
(3) hydrolysis in base (4) rxn w/ Ce(IV)
(5) hydrolysis in acid (6) rxn w/ Fe(III)
(7) rxn w/ Ag⁺ (8) rxn w/ HCl/ZnCl₂
(9) rxn w/ Br₂ in water (10) rxn w/ 2,4-DNP
(11) rxn w/ iodine in HO⁻ (12) rxn w/ hydroxylamine
(13) rxn w/ NaI in acetone (14) rxn w/ semicarbazide
(15) rxn w/ Fe(Fe(SCN)₆) (16) rxn w/ AlCl₃/CHCl₃
(17) rxn w/ PhSO₂Cl (18) rxn w/ Mg/ether
(19) rxn w/ Cu/flame (20) rxn w/ Br₂/CCl₄
(21) rxn w/ MnO₄⁻ (22) rxn w/ Fe(OH)₂
(23) ignition (24) rxn w/ HNO₃/H₂SO₄
(25) rxn w/ 3,5-dinitrobenzoyl chloride
(26) rxn w/ benzoyl chloride

>7, 11, 19, 23, 6, 16

*On reaction with Fe(III), had the unknown been reacted with hydroxylamine previously (y/n)?

>n

*On reaction with Fe(III), did you observe any of the following: solution turned blue (b)/ solution turned clear (c)/ solution turned red/purple (r)/ no change (n)?

>r

*On reaction with silver nitrate were any of the following observed: pale solid precipitated (s)/ colored solid precipitated (c)/ solution heated up (h)/ no reaction (n)

>s

Did the solid precipitate redissolve on addition of dilute sulfuric acid (y/n/x)?

>x

*On reaction with iodine in basic solution, was a solid precipitate formed (y/n/x)?

>n

*On reaction with aluminum chloride and chloroform, was a color observed (y/n)?

>n

*On heating with copper wire in a flame, was a colored "flash" observed (y/n)?

>y

*On burning the sample in a flame, were any of the following observed: soot (s)/ yellow flame (y)/ green "flash" (g)/ blue or clear flame (b)/ white ash (a)?

>b

*Do you wish to run through the list of questions to correct your responses (y/n)?

>n

*Type all the numbers which correspond to the families whose functional groups you believe may be present:

(1) alcohol (2) aldehyde
(3) enol (4) ketone
(5) phenol
(6) carboxylic acid (7) acid chloride
(8) acid anhydride (9) ester
(10) amide (11) nitrile
(12) amine (13) nitro
(14) ether (15) alkane
(16) alkyl halide (17) alkene / alkyne
(18) aryl halide (19) aromatic hydrocarbon

>3, 5, 16, 18

*Which table would you like to examine first: enols (3), phenols (4), ketones (3), alkyl halides (16), aryl halides (18), none (n) ?

>4

*You observed a boiling point of 155 for this compound: what range of boiling points do you want to see?

>150-160

*No phenols boil within the range you have selected! Do you want to look at other compounds (x) or change the boiling range (b)?

>x

*Which table would you like to examine first: enols (3), phenols (4), ketones (3), alkyl halides (16), aryl halides (18), none (n) ?

>3

*You observed a boiling point of 155 for this compound: what range of boiling points do you want to see?

>150-160

-->this would be a display from the database<--

enol	bp	dnp mp	oxime mp	semi-C mp
4-methyl-3-oxo-				
pentanenitrile	159			
2,4-hexanedione	160			
3-oxohexanenitrile	160			

*Do you wish to choose one or look again (c/a) ?

>a

*Do you wish to look at the same table again or go to a different table (s/d) ?

>d

*Which table: alkyl halides (16), aryl halides (18), none (n) ?

>16

*You observed a boiling point of 155 for this compound: what range of boiling points do you want to see?

observed. Changes include decolorization of the reagent, color changes, precipitates, separation of layers, heat evolution, gas evolution, charring:

rxn w/ acidic Cr(VI)	rxn w/ Br ₂ in water
rxn w/ Ce(IV)	rxn w/ 2,4-DNP
rxn w/ Fe(III)	rxn w/ hydroxylamine
rxn w/ Ag ⁺	rxn w/ semicarbazide hydrochloride
rxn w/ HCl/ZnCl ₂	rxn w/ 3,5-dinitrobenzoyl chloride
rxn w/ iodine in HO ₂	rxn w/ benzoyl chloride

*Write the balanced chemical equation and draw the structural formula of the product for any derivatives which you have made from your unknown compound:

*Was the derivative recrystallized?

*Melting point was obtained for the derivative?

*Functional groups do you believe may be present:

alcohol aldehyde enol
ketone phenol carboxylic acid
acid chloride acid anhydride ester
amide nitrile
amine nitroalkane
ether alkane alkyl halide
alkene/alkyne aryl halide aromatic hydrocarbon

*Name the compound you believe your unknown to be and draw the structural formula:
